

Modified Nanostructure MgO Superbasicity with CaO in Heterogeneous Transesterification of Sunflower Oil

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MODIFIED MgO superbasicity with CaO as nanostructure were prepared by hydration-dehydration method and used as heterogeneous catalyst for the synthesis of biodiesel (FAME) via the transesterification of sunflower oil with methanol. The synthesis of biodiesel was characterized by proton nuclear magnetic resonance ($^1\text{H-NMR}$) and attenuated total reflectance (ATR). The catalyst was characterized by Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA-DTG) and nitrogen gas adsorption (NA). The basicity of the prepared catalyst samples was also studied by back titration method. The optimal produced biodiesel was 97% at 25% molar ratio which carried out at atmospheric pressure, reaction time of 3 h, a reaction temperature of 65°C, a catalyst amount of 5 wt% and methanol: oil molar ratio of 9:1. The percentage conversion of biodiesel was determined by $^1\text{H-NMR}$. The modified nanostructure MgO with CaO showed tremendous potential in large-scale biodiesel from sunflower oil.

Keywords: Transesterification, Biodiesel, Sunflower oil, Nanostructure heterogeneous catalyst, Calcium oxide, magnesium oxide.

Introduction

Biodiesel is “an ester based renewable and biodegradable form of fuel which consists of mono-alkyle esters of fatty acids derived from vegetable oil such as sunflower oil[1]. Biodiesel has several advantages comparing to petrodiesel such as high flash point, low viscosity, and less carbon dioxide emission[2]. Traditionally, biodiesel is produced by using transesterification process, as the physical characteristics of fatty acid esters are very similar to the petrodiesel, and the process is comparatively simple. It has been commonly used to reduce the high viscosity of triglycerides[3-6].

Generally, transesterification is a catalyzed chemical reaction of vegetable oil (or animal fat) and short chain alcohols (methanol or ethanol) in the presence catalyst[7]. Commonly, there are three types of catalyst that are used in biodiesel production. Among them are the heterogeneous catalysts which are most widely used because they are non-corrosive, spreadable, and recyclable. Various solid base heterogeneous catalyst gave been used in transesterification reaction. Since they are active in this reaction at the temperature

around boiling point of methanol[8]. The order of activity for the alkaline earth oxide catalyst is $\text{BaO} > \text{SrO} > \text{CaO} > \text{MgO}$ [9]. Among the several solid base heterogeneous catalysts are CaO and MgO metal oxide were investigated by many researchers for biodiesel production from sunflower oil.

Calcium oxide (CaO) is one of the alkaline earth oxide catalysts that was displayed higher transesterification activity[10,11]. The application of CaO for biodiesel production from vegetable oil according to its natural source was investigated by many researchers[12-18].

Magnesium oxide (MgO) is a solid and basic material. It is not dissolved in the reaction medium. MgO showed a good yield of biodiesel from sunflower [19,20]. Mixed metal oxide catalysts have attracted an increased amount of attention because of their tunable basicity using modification of their chemical composition and synthesis procedure [21-23]. Taufiq et al. [24] studied the physiochemistry and catalytic properties of the CaMg mixed oxides. Further study was done by Limmanee et al.[21], they used a series of mixed oxides of Ca, Mg, and Zn. Lukić

et al.[25]investigated the kinetics of the sunflower and used vegetable oil methanolysis catalyzed by using mixed CaO.ZnO. Moreover, Wen et al. [26] studied the biodiesel production from waste cooking oil using TiO₂-MgO mixed oxides.

In this study, the preparation of modified MgO superbasicity with CaO as nanostructure using hydration-dehydration method for biodiesel synthesis from sunflower oil has been investigated by comparing different MgO-CaO molar ratios.

Experimental

Materials

Refined sunflower “oil which is used in the experiment was purchased from a local supermarket. The sunflower oil fatty acid contents are listed in Table 1. Methanol (99.8%) was obtained from Merck KGaA. The MgO and CaO were supplied by the department store and both of them are from LAB Grade”.

TABLE 1. Fatty composition of sunflower oil

Fatty acid	Composition
linoleic acid	63.4
oleic acid	24.6
palmitic acid	6.1
stearic acid	4.2
others	1.7

Catalyst Preparation

Surface “modified MgO superbasicity with CaO as nanostructure with different molar ratios were prepared by hydration-dehydration method[27]. A commercial magnesium oxide (CM-MgO) and commercial calcium oxide (CM-CaO) as starting materials and modification from oxide-compounds to hydroxide-compounds were done using distilled water (D.W.). The catalyst samples were prepared by thermal decomposition of the sample which contains magnesium hydroxide (Mg(OH)₂) and calcium hydroxide (Ca(OH)₂) at 600°C. For example, molar ratio of 1:0.05 (MgO: CaO) was prepared by taking 4 gm from CM-MgO and 0.28 gm from CM-CaO, then this sample was dispersed in 53.3 ml D.W. and refluxed for 16 h at 90-95°C to produce Mg(OH)₂-Ca(OH)₂, after that the precipitate was collected by filtration and dried in oven at 100±5°C for 4-5 h to remove

excess of water. This step is called the hydration method. Then the dried Mg(OH)₂-Ca(OH)₂ was ground using mortar and pestle to form a fine powder of sample. The next step, dehydration method, was performed to promote the formation of nanostructure oxide MgO-CaO by calcinations in furnace at 600°C for 2 h. After that the nanostructure sample as a catalyst was kept in glass bottle in desiccators that contain silica gel pellets”.

Catalyst Characterization

Thermogravimetry-Derivative Thermogravimetry Analysis

Thermal decomposition of the catalysts was evaluated “by thermogravimetric analysis-different thermal analysis (TGA-DTG). It was used to study the decomposition of Mg(OH)₂ and Ca(OH)₂. It carried out on a ceramic crucible in the GT analyzer. Metler-Toledo Q100 instrument operation under the following conditions. First, flow of air atmosphere 10cm³ m⁻¹, second, heating rate 10°C min⁻¹, and third, temperature from room temperature 25-800°C.

Fourier-Transfer Infrared Analysis

A Fourier- transfer infrared (FTIR) measures the absorbance of infrared (IR) laser light by chemical bonds in a sample. FTIR spectra of the samples were recorded in a Perkin Elmer Infrared Spectrometer in the range of 400-4000cm⁻¹. A standard KBr powder was used for preparing the solid samples. This technique was used to identify the functional group presence in MgO (600°C) and five molar ratios (MgO: CaO) (600°C).

Nitrogen Gas Adsorption Analysis

The specific surface area of the prepared catalyst in different molar ratios at 600°C was carried out by nitrogen physisorption according to the single-point BET (Brunauer-Emmett-Teller) method using the apparatus plus chemosorb 2750. The instrument operates in a single-point mode. Before the measurement the samples were dried at the temperature 105°C for about 2 h to remove the absorbed water from the atmospheric humidity. Surface characteristics of the catalyst base on physical adsorption of nitrogen at the temperature of liquid nitrogen.

Basic Strength Nanostructure Mixture (Back Titration)

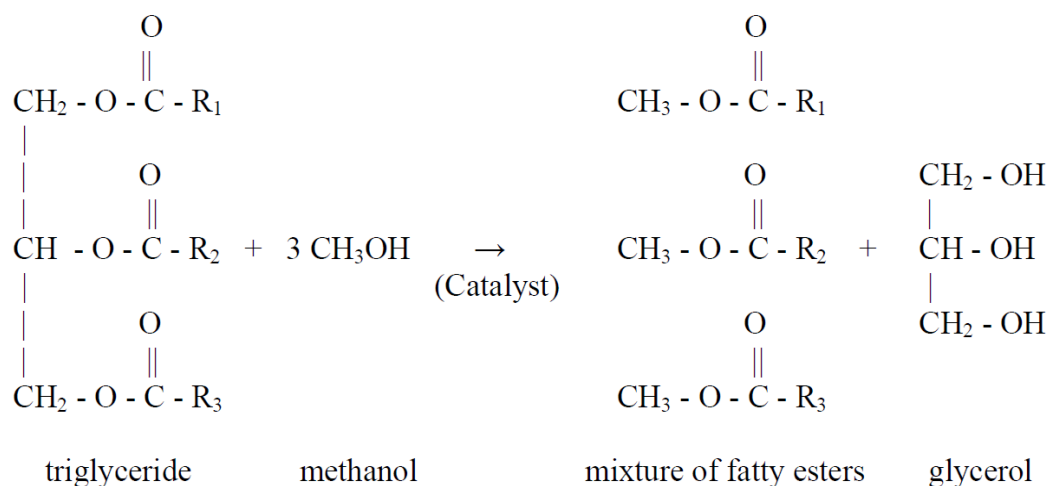
The basicity of the catalyst was studied by back titration method (measurement of the

aqueous-soluble basicity). Approximately, 0.1gm of sixsamplesMgO-CaO 600°C was shaken in 10ml of distilled water and leave for 24h". Then the obtained slurry was separated by using centrifuge (3000rpm) for 15min, after that the resulting solution was further neutralized by using 10 ml of 0.5M HCL. Finally, the residue acid was titrated with 0.02M NaOH with phenolphthalein which used as an indicator.

Transesterification Procedure

Transesterification reaction "was carried out in a 100ml round-bottomed flask equipped with a thermometer, reflux condenser, and magnetic stirrer, and the round-bottomed flask was immersed in an oil bath. The reaction procedure was as follows: first, the catalyst was dispersed

in methanol under magnetic stirring. Then, the sunflower oil was added into the mixture and heated. The amount of the raw material was 11ml of sunflower oil, 2.4 ml of methanol, and 5 wt% of catalyst. Three reaction conditions were as follows: 9:1 molar ratio of methanol: oil, reaction temperature of 65°C, and reaction time 3 h at atmospheric pressure. After the products were centrifugated at 3000 rpm for 15 min, it formed three layers. The upper layer was the excess methanol, the middle layer was the biodiesel and the bottom layer was for the solid catalyst and a small amount of glycerol. After that the biodiesel was collected for characterization". The scheme of the transesterification reaction of triglyceride with methanol is given as:



Biodiesel Characterization

Proton Nuclear Magnetic Resonance

"Proton nuclear magnetic resonance (¹H-NMR) is a spectroscopic method (physical occurrence), which was used to study the properties of molecules which contain magnetic nuclei by applying a magnetic field and observation the frequency [28, 29]. It is useful technique to determine completely the structure and the chemical group composition of the sunflower oil and the biodiesel. Typically, samples were made of 0.05 ml of biodiesel dissolved in 0.5 ml chloroform-d(CDCL₃) and recorded in ¹H-NMR spectrometry model Burker advance II 400 MH₂, by placing the sample in a magnetic field and NMR active nuclei such as ¹H will absorb electromagnetic radiation at frequency characteristic of the isotope. The energy of the absorption and the intensity of the signal are

proportional to the strength of the magnetic field.

Attenuated Total Reflectance

An attenuated total reflection (ATR) accessory operates by measuring the changes that occur in totally internally reflected infrared beam when the beam comes into contact with a sample. The major benefit of ATR is the ability to measure a wide variety of solid and liquid samples without complex preparation. This technique was used to identify the chemical composition of the biodiesel was recorded in Perkin Elmer instrument spectrometer by putting a drop of sample on the diamond crystal and start the measurement. The produced spectrum of the sample will be in the range of 650-4000cm⁻¹. The ATR was cleaned with methanol after every sample analysis.

Results and Discussion

Catalyst Characterization

TGA-DTG Analysis

TGA-DTG analysis was used to study the thermal behavior of $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$. The results were presented in Fig. 1 and 2, respectively. From TGA-DTG curves we can determine the optimum calcinations temperature for the preparing CaO and MgO. The TGA-DTG curves of $\text{Ca}(\text{OH})_2$ in Fig. 1 shows many events of mass losses. The first mass loss (1%) occurs between 50-100°C, is attributed to the desorption of humidity on the exterior surface of the $\text{Ca}(\text{OH})_2$. The residual water can be desorbed from the surface during heating the sample by TG analyzer. The second mass loss (19.60%) occurs between 400-500°C, which is representing the major weight loss. This is attributed to the released chemisorbed water molecule and assigned as the mixture of strong basic centers derives O^{2-} ions adjacent to OH^- ions. Moreover, there is no mass loss between 500-620°C and this is attributed to the complete decomposition of $\text{Ca}(\text{OH})_2$ and the formation of CaO. Finally, mass loss about 8% occurs between 620-730°C and this is most probably due to restructuring of the morphological structure of CaO and carbonated impurities. In DTG curve the exothermic peak at 460°C is attributed to the

initial decomposition of $\text{Ca}(\text{OH})_2$ to CaO and H_2O . The TGA-DTG results for $\text{Ca}(\text{OH})_2$ indicate that the optimum calcinations temperature to produce the nanostructure CaO can be done at 600°C.

The TGA-DTG curves of $\text{Mg}(\text{OH})_2$ in Fig. 2 shows many regions of weight losses. The first weight loss (7.48%) occurs between 40-100°C, is attributed to the removal of water, which is physically adsorbed onto the surface of the material and hydroxyl group attach to Mg^{+2} at the surface. Furthermore, a continuous weight loss of $\text{Mg}(\text{OH})_2$ occurs when the temperature increases until 420°C where the weight loss had been stable. The second weight loss (22.78%) occurs between 300-420°C, which is representing the major weight loss. This is attributed to the beginning of the decomposition of $\text{Mg}(\text{OH})_2$ to produce MgO, while water molecule released as product, and assigned as the mixture of strong basic centers derives O^{2-} ions adjacent to OH^- ions.

At Final, no weight loss occurs between 420-800°C and this is most probably due to the complete decomposition of $\text{Mg}(\text{OH})_2$ and the formation of MgO. In DTG curve, the exothermic peak at 400°C is attributed to the beginning of the decomposition of $\text{Mg}(\text{OH})_2$ to MgO and H_2O . The TGA-DTG results for $\text{Mg}(\text{OH})_2$ indicate that the optimum calcinations temperature to produce the nanostructure MgO can be done at 600°C.

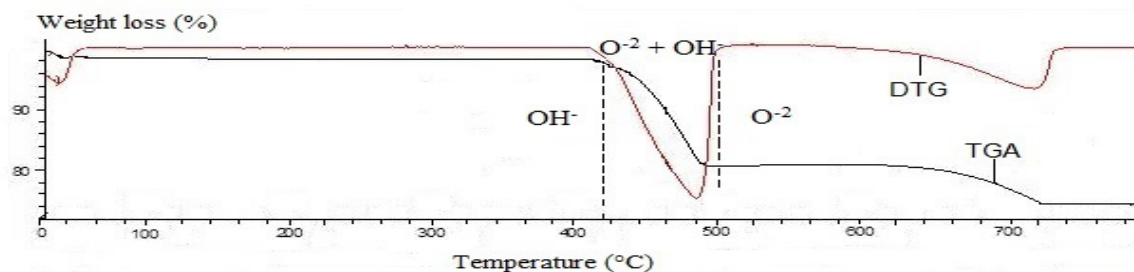


Fig. 1. TGA-DTG curve of the $\text{Ca}(\text{OH})_2$ precursor.

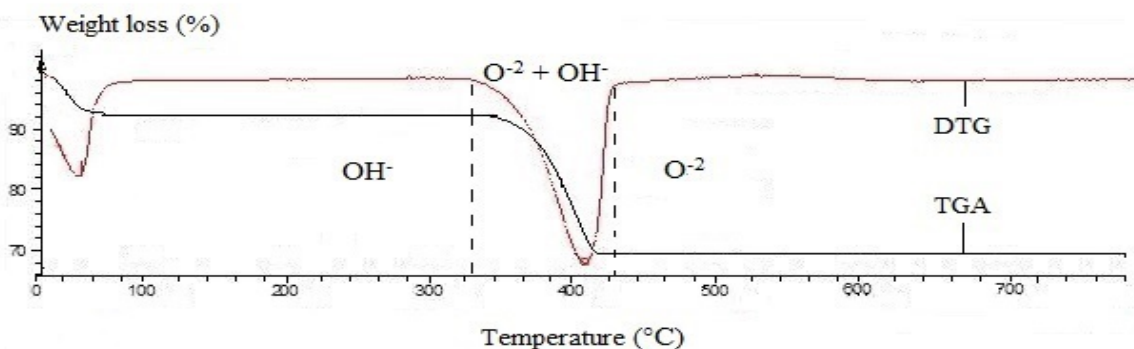


Fig. 2. TGA-DTG curve of the $\text{Mg}(\text{OH})_2$ precursor.

FTIR Analysis

The FTIR of the samples at different molar ratios of 1:0.05, 1:0.10, 1:0.15, 1:0.20, 1:0.25, and 1:0.30 which calcined at 600°C were measured after drying at 105°C to remove most of the adsorbed moisture. The FTIR spectra for the samples are presented in Fig. 3. There are two types of OH bonding appear at FTIR spectra for the samples. First, is the unassociated hydroxyl groups will be appeared as sharp peaks at 3644.51 cm⁻¹ for the stretching mode and peaks at 1440.3 cm⁻¹ for the bending mode. And secondly, the water molecules physisorbed on the surface of the samples will be appeared as broad peaks at 3439.9 cm⁻¹ for the stretching mode and peaks at 1637.3 cm⁻¹ for the bending mode.

These absorptions were attributed to hydroxyl species resulting from a fast reaction between the atmospheric moisture and the samples. These bands had been previously characterized by several researches[30]. Moreover, the presence of impurities carbonates on CaO surface in the samples that band at 874.06 cm⁻¹ is corresponding to the vibration mode of the carbonate species. In addition, the deformation vibration of O²⁻ is appeared as broad peaks at 673.04 cm⁻¹ for the deformation mode. In Fig. 3, the intensity of the bands at 3644.51 cm⁻¹ increased between 1:0.10 and 1:0.30 and disappeared at 1:0.05, this phenomenon may be attributed to the increasing concentration of CaO in the prepared samples, which is considered a hygroscopic compound.

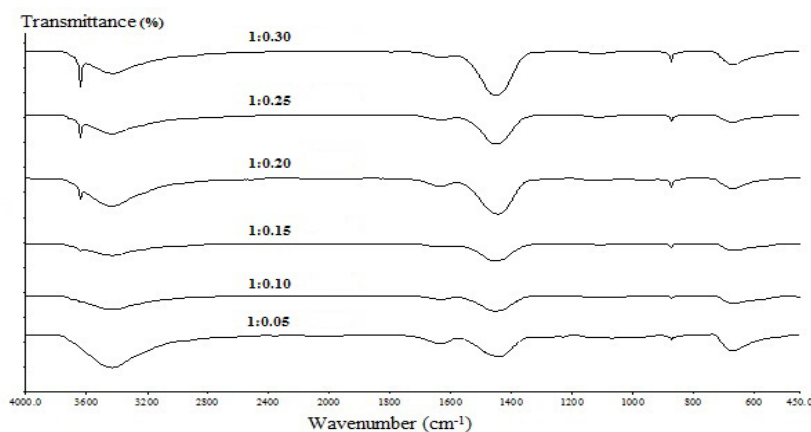


Fig. 3. FTIR spectra for the prepared nanostructure samples at 600°C.

Back Titration

The basicity of the prepared molar ratios of nanostructure samples was recorded by back titration at 600°C, since we have obtained the high basicity for CaO and MgO at 600°C respectively. Figure 4 shows the basicity of the prepared

nanostructure MgO and the prepared samples. The basicity of the prepared samples increases when the concentration of the CaO increases comparing with the basicity of the prepared nanostructure MgO. This is most probably happening because that CaO is considered super base catalyst.

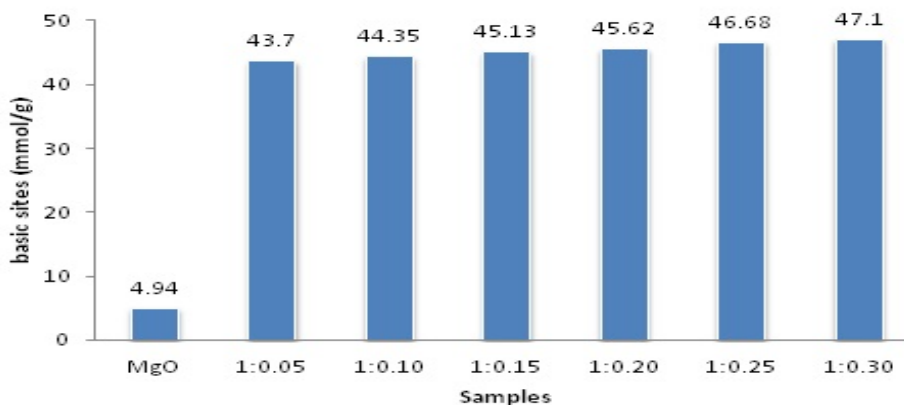


Fig. 4. Basicity of the prepared nanostructure MgO and MgO: CaO samples at 600°C.

NA Analysis

The BET surface areas of the different molar ratios of the prepared nanostructure catalyst of 1:0.05, 1:0.10, 1:0.15, 1:0.20, 1:0.25, and 1:0.30 which calcinations at 600°C. The results are summarized in Table 2. The minimum surface area (S_{BET}) of the catalyst was 47.86 m²/g at 1:0.05, whereas the maximum S_{BET} of the catalyst was 84.69 m²/g at 1:0.25. In addition, the S_{BET} is increased until 1:0.25; this is due to increasing the gaps on the surface area of the samples which contributes to increasing the efficiency of the samples in many chemical reactions. Whilst the S_{BET} at 1:0.30 is decreased comparing with 1:0.25, although the molar ratio of the sample is greater than 1:0.25. This phenomenon may be attributed to the occurrence of the agglomerated which causes the pore to appear narrow which reduces the porosity of the surface and then causes decreasing the surface area of the sample.

TABLE 2. BET analysis results for the prepared nanostructure samples calcined at 600°C

Samples	S_{BET}
CaO	20.25
MgO	42.01
1:0.05	47.86
1:0.10	59.79
1:0.15	69.52
1:0.20	69.57
1:0.25	84.69
1:0.30	61.67

Biodiesel Characterization

¹H-NMR Analysis

NMR is a spectroscopic method which gives information about the number of magnetically distinct atoms of the type being studied. From the present study the sunflower oil and the biodiesel are characterized by using ¹H-NMR. The position of each peak on the ppm scale of the spectrum is an indication of the position of the protons in the chemical structure associated with each peak.

The ¹H-NMR spectrum oil in Fig. 5 shows the results of typical protons. We observed the peaks at 0.8-0.9 ppm due to the terminal methyl protons (-CH₃). The peaks at 1.27-1.41 ppm are characterized of methylene protons (-C-CH₂-C-), the peak at 1.62 ppm raising from β-carbonyl

methylenes (-CH₂-CH₂-CO-O-), the peak at 2.02, 2.8, and 5.3 ppm associated to unsaturation are characteristic of allylic, bis allylic and vinyl (olefine) hydrogen respectively. A triplet of α-carbonyl methylenes proton (α-CH₂) at 2.3 ppm. The peaks appear at 4.1-5.4 ppm due to H-1, H-2, and H-3 peaks indicate to the protons attached to glycerol carbons.

If we compared the spectrum of sunflower oil before methanolysis in Fig. 5 with the spectra of biodiesel in Fig. 6 which showed a similar chemical group composition. However, the difference between the spectra indicates the presence of more saturated molecules in the biodiesel comparing to sunflower oil, and showed initially present in the spectrum of sunflower oil at 4-4.3 ppm is no longer present in all the samples of biodiesel, this is an indication of triglyceride break down into smaller chain and also indication high conversion yield of sunflower oil into methyl esters [31].

In addition, we observed two peaks are the distinct peak for the confirmation of methyl esters in the biodiesel, the signal at 3.68 ppm (methoxyl groups of methyl esters) and the signal at 2.3 ppm (α-carbonyl methylenes proton (α-CH₂) of all fatty acid derivatives). ¹H-NMR can also be used to calculate the conversion of oil to methyl esters by transesterification reaction[28] [29]. The relevant signals chosen for integration were those of methoxyl group in the methyl esters at 3.68 ppm (the strong singlet peak and the α-carbonyl methylenes proton at 2.3 ppm) (the triplet peak).

A straight forward equation used to calculate the yield of transesterification reaction is

$$C=100*(2A_{\text{ME}}/3A_{\alpha\text{-CH}_2}) \quad (1)$$

where C is the conversion yield of sunflower oil to methyl esters, A_{ME} is the integration value of the protons of the methyl esters and $A_{\alpha\text{-CH}_2}$ is the integration value of the α-methylene protons. The factors 2 and 3 derive from the fact that the methylene carbon possesses two protons and the alcohol (methanol-derived) carbon has three attached protons.

The yield of fatty acid methyl ester (biodiesel) is calculated by using Eq.1. The relationship between the yield of biodiesel and the nanostructure mixture molar ratios are presented in Fig.7.

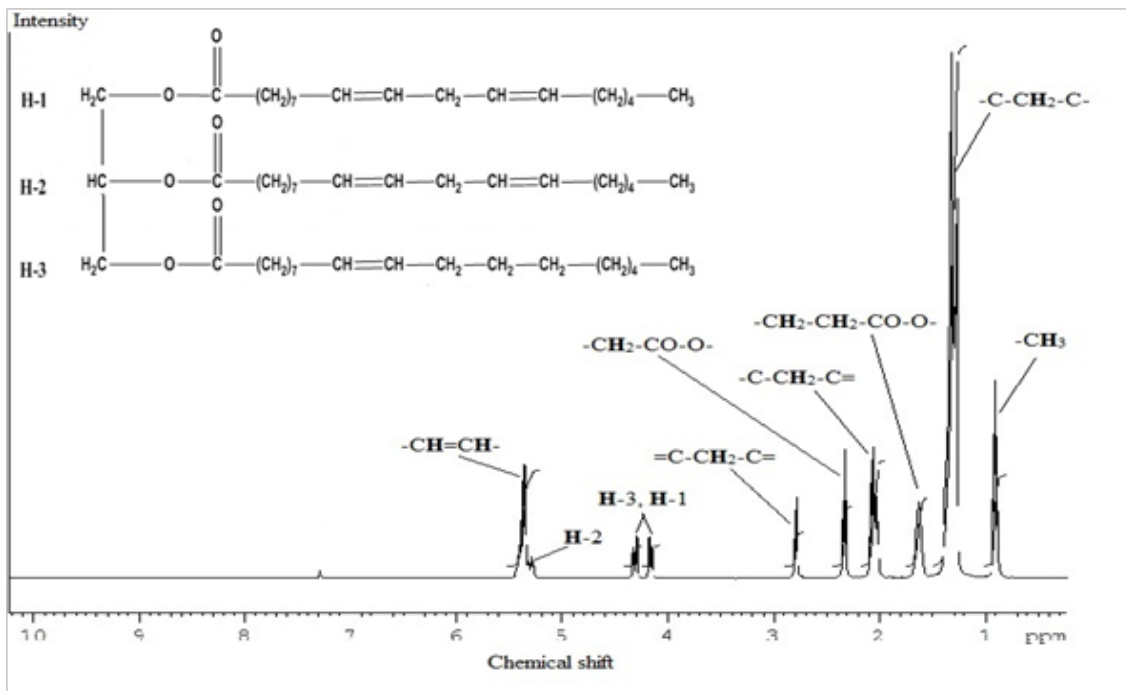


Fig. 5. ¹H-NMR spectrum of sunflower oil.

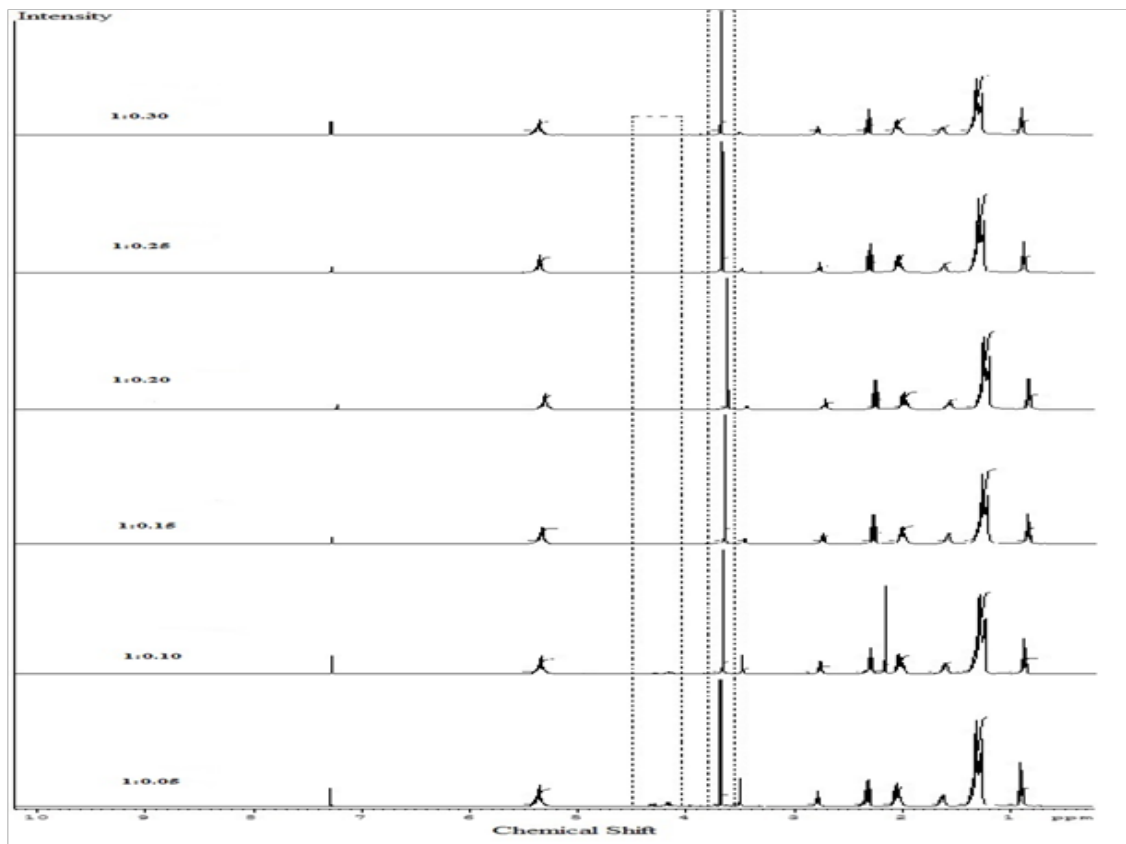


Fig. 6. ¹H-NMR analysis of FAME derived from sunflower oil for various nanostructure mixture molar ratios.

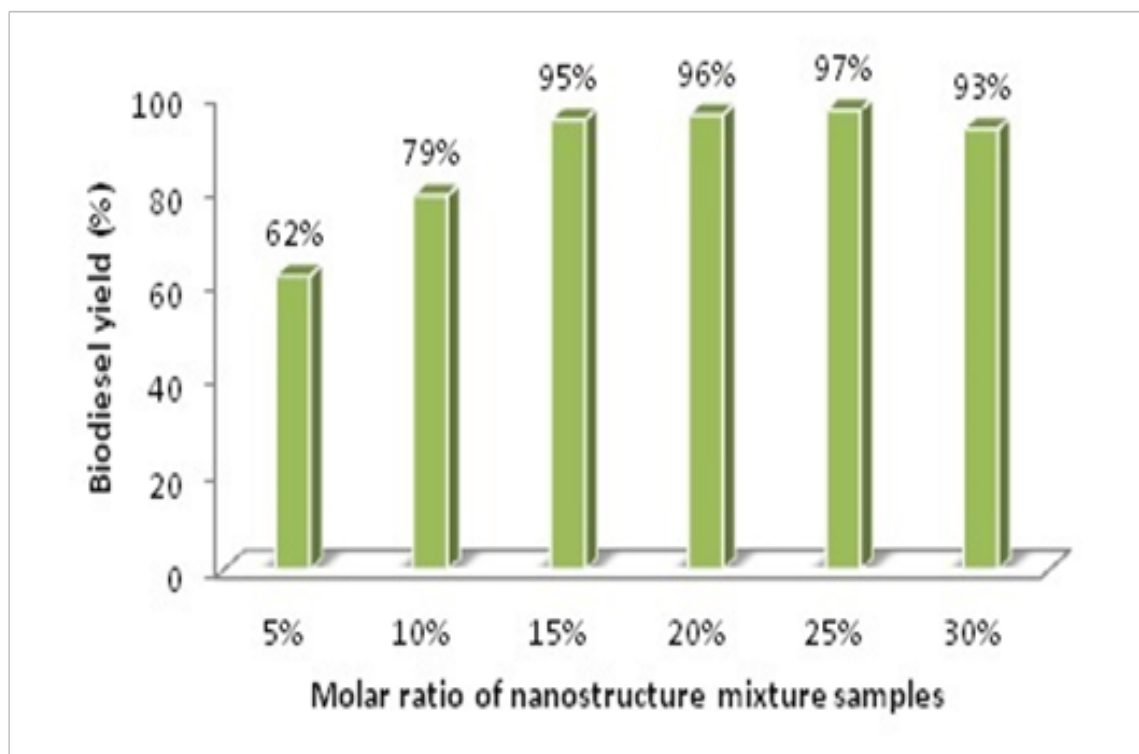


Fig. 7. The relationship between the yield of biodiesel and the nanostructure mixture molar ratios.

From Fig. 7 we observed that the yield of biodiesel increases when the percentage of molar ratio for the mixture increases up to 1:0.25 which achieved the higher yield of the biodiesel. In addition, we observed that the yield of the biodiesel decreases when the molar ratio is 1:0.30. This phenomenon is attributed to the fact that the surface area of the catalyst at 1:0.30 decreased compared with the surface area of the catalyst at 1:0.15, 1:0.20, and 1:0.25. This result supported the previous NA discussion.

ATR Analysis

ATR is an IR sampling technique that identifies the functional groups and bands that are corresponding to stretching vibration in the sunflower oil and biodiesel samples. The changes of the carbonyl function group to the methoxyl carbonyl group attributed to the transesterification reaction had occurred and that fatty acid methyl ester (FAME) has been produced. In this analysis, the formation and loss of functional groups between sunflower oil and FAME (biodiesel) were identified by using ATR.

The ATR spectra that appear the comparison between sunflower oil and the biodiesel which prepared from 5% molar ratio as a catalyst

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and 1:9 molar ratio of oil: methanol are shown in Fig. 8. The sunflower oil absorption peak was identified at 1098.09 cm^{-1} this indicated the C-CH₂-O vibration. The biodiesel shows a peak at 1195.03 cm^{-1} , which can be attributed to the O-CH₃ initial methyl group stretch and the peak at 1436.27 cm^{-1} comes from the -CH₃ asymmetric bending vibration.

Moreover, we observed the broad peak at 3369 cm^{-1} was presented in biodiesel spectrum due to the presence of small amount of the O-H group which comes from two sources of methanol, the first is from methanol in the transesterification reaction of oil to biodiesel and the second is from methanol which had been used as cleaning agent at the sample holder of ATR. The results of ATR peaks for the functional group of oil (TG) and the biodiesel (FAME) are summarized in Table 3.

ATR results confirm that biodiesel was successfully prepared from transesterification of sunflower oil.

Conclusion

Nanostructure MgO-CaO mixed oxides catalyst with different molar ratios, which synthesized by the hydration-dehydration method,

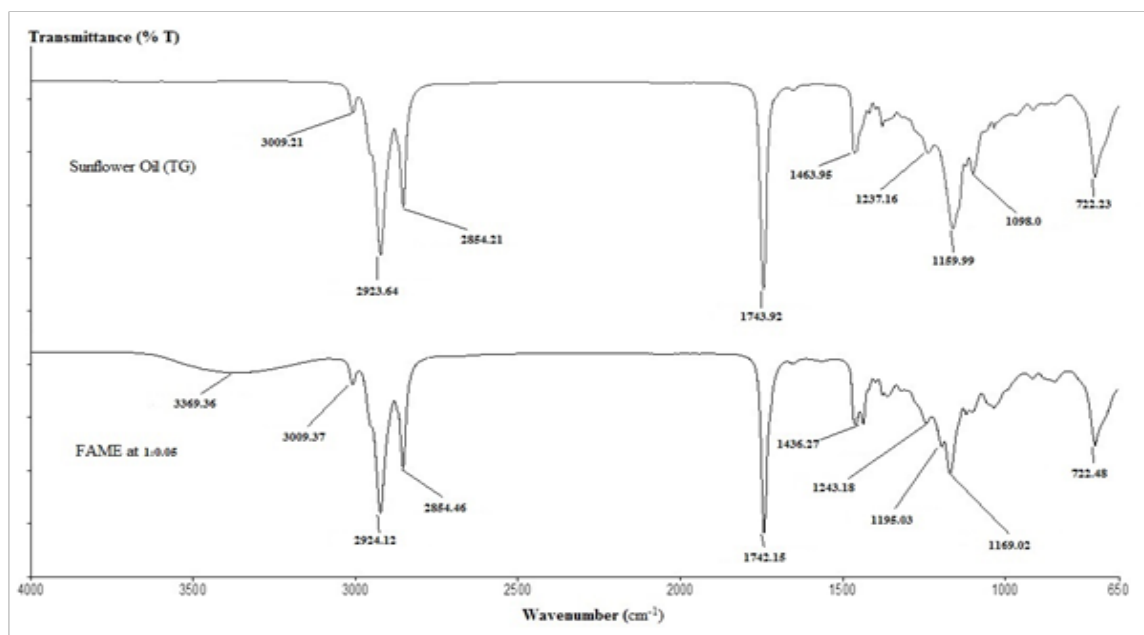


Fig. 8. Comparison of sunflower oil with the biodiesel spectra.

TABLE 3. Comparison of the band position between TG and FAME.

Band Position (cm ⁻¹)	Assignment	TG	FAME
3369	-OH stretching	-	+
3009	-OH stretching	+	+
2924-2854	C-H SP ³ stretching	+	+
1742	C=O stretching	+	+
1436	-CH ₃ stretching	-	+
1243-1169	C-O-C sym. stretching	+	+
1195	O-CH ₃ stretching	-	+
1098	C-CH ₂ -O stretching	+	-
722	(CH ₂) _n stretching	+	+

ATR results confirm that biodiesel was successfully prepared from transesterification of sunflower oil.

has been successfully prepared and characterized for the transesterification of sunflower oil with methanol in biodiesel production. The influence of the mixture metal oxides on the yield of biodiesel production was studied using 5%, 10%, 15%, 20%, 25%, and 30% molar ratios of MgO and CaO. It was possible to observe how the amount of CaO increased the strength of basicity for the samples, also it can be observed a direct influence between the specific surface area of the nanostructure mixture and the yield of the biodiesel. In addition, increasing the specific surface area of the catalyst will increase

the biodiesel yield. At this studied conditions, a maximum yield of 97% of biodiesel at 25% molar ratio can be obtained at mild condition (temperature at 65°C and atmospheric pressure). The nanostructure mixed oxides catalyst, MgO-CaO, showed tremendous potential in large scale biodiesel production from sunflower oil".

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تحسين قاعدية مركب اوكسيد المغنيسيوم MgO مع اوكسيد الكالسيوم CaO ذو التركيبة النانوية في عملية نقل الاستر الغير متجانس في زيت زهرة عباد الشمس

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في هذا البحث تم تحضير البايوديزل (الوقود الحيوي) من زيت زهرة عباد الشمس باستخدام طريقة نقل الاستر وبالاعتماد على تحسين القاعدية لمركب اوكسيد المغنيسيوم MgO مع اوكسيد الكالسيوم CaO كتركيب نانوي والذي تم تحضيرهم بطريقة hydration-dehydration كعامل مساعد غير متجانس. تم تشخيص البايوديزل الناتج باستخدام تقنية التحليل الطيفي بالرنين النووي المغناطيسي (H-NMR) وكذلك باستخدام تقنية الموهن اجمالي الانعكاس (ATR). كذلك تم تشخيص العامل المساعد باستخدام ثلاثة تقنيات وهي مقياس الطيف باستخدام متحول فورييه في مجال الاشعة تحت الحمراء وتقنية التحليل الوزني الحراري (TGA-DTG) وتقنية امتزاز غاز النتروجين (NA) لتوضيح الخواص السطحية والتشكيلية للعامل المساعد، وقد درست قاعدية العامل المساعد المحضر باستخدام طريقة التسحيح الرجعي. تم الحصول على افضل انتاجية للبايوديزل وبنسبة 97% تحت الضغط الجوي عند الظروف المثلى وهي 25% نسبة مولارية، وزمن تفاعل بمقدار 3 ساعات، وعند درجة حرارة 60°C، وكمية عامل مساعد بنسبة 5 wt% واخيرا النسبة المئوية للميثانول الى الزيت بمقدار 1:9. من خلال هذه النتائج لاحظنا ان التحسين الذي اجريناه للعامل المساعد MgO باستخدام CaO له امكانية رائعة لانتاج مدى واسع من البايوديزل باستخدام زهرة عباد الشمس.